Southern Fine Particulate Monitoring Project

Sixth Quarterly Progress Report

Reporting Period: January 1 – March 31, 2002

Issued: April 2002

DOE Cooperative Agreement No. DE-FC26-00NT40770

Submitted to

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Abstract

This quarterly report presents results and analysis of continuous onsite ambient fine particulate data at the North Birmingham sampling site during the January – March, 2002 study period. The continuous data include $PM_{2.5}$ mass concentrations measured by TEOM, particle sulfate using the R&P 8400S monitor, particle size distributions measured by SMPS and APS monitors, and $PM_{2.5}$ light scattering extinction coefficient as measured by nephelometer. Some instrumental issues were noted with the upgrade of the APS model 3320 are described in the report, as well as preliminary performance indications for the upgraded instrument. During the quarter preliminary data analysis and modeling studies were conducted to test the potential of the North Birmingham site data for source attribution analyses. Our initial assessment has continued to be optimistic in this regard due to the location of the site relative to several important classes of local and midrange emission sources. We anticipate that these analyses will provide good separations of the effects of major source classes and spatial source clusters, and will provide useful information relevant to $PM_{2.5}$ implementation strategies.

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Introduction

This is the sixth quarterly progress report of the "Southern Fine Particulate Monitoring Project", funded by the U.S. Department of Energy's National Energy Technology Laboratory under DOE Cooperative Agreement No. DE-FC26-00NT40770 to Southern Research Institute (SRI). In this two year project SRI will conduct detailed studies of ambient fine particulate matter in the Birmingham, AL metropolitan area. Project objectives include:

- $ Augment existing measurements of primary and secondary aerosols at an established urban southeastern monitoring site
- $ Make a detailed database of near-continuous measurements of the time variation of fine particulate mass, composition, and key properties (including particle size distribution)
- $ Apply the measurements to source attribution, time/transport properties of fine PM, and implications for management strategies for $PM_{2.5}$
- $ Validate and compare key measurement methods used in this study for applicability within other $PM_{2.5}$ research by DOE-FE, EPA, NARSTO, and others.

Summary of Technical Progress

Progress and Plans

During the sixth project quarter, continuous onsite ambient data were collected and monitored. Details include:

- $ January measurement intensive with Eastern Supersite Program
- $ Onsite comparative measurements with particulate sulfate monitor R&P 8400S and SEARCH Particulate Composition Matter (PCM) results
- $ Prepare July data in general format for modeling study
- $ Comparison of results for the original TSI APS 3320 to the upgraded APS 3321
- $ Continued field testing for particulate sulfate monitor of Harvard design
- $ Continued monitoring with TEOM, particle sizing instruments, R&P 8400 Sulfate monitor, Radiance M903 Nephelometer, and 43CTL Sulfur Dioxide analyzer
- $ Source attribution analysis using wind trajectories
- $ Preliminary results presented at DOE - sponsored *$PM_{2.5}$ and Electric Power Generation Conference,* April 9-10, 2002 in Pittsburgh, PA.

Plans for next quarter include the following:

- $ Continue source attribution analysis using wind trajectories, receptor methods
- $ Continue onsite monitoring with continuous monitoring instruments
- $ Continue analysis of initial continuous particulate data

Problems and Assessment for Future Progress

The APS 3320 was sent to TSI to be upgraded to an APS 3321 in mid January. Once the

instrument returned to SRI, the 3321 was tested in our laboratory and redeployed to the North Birmingham site in mid February. Also in mid February, the motherboard and power supply shorted in the computer dedicated to acquire the raw data from each instrument. A minimal amount of data was lost before a replacement computer was put into place. The vacuum pump of the 8400S Sulfate monitor was removed and rebuilt in the end of February. Three weeks after the pump had been rebuilt, the pump failed and had to be replaced. Again, a minimal amount of data was lost before a replacement pump was installed. The SMPS was removed from the North Birmingham station mid February and for the majority of March. The instrument was utilized in field tests for other scheduled SRI projects.

Experimental

The APS 3320 was sent to TSI to be upgraded to an APS 3321 January 23. Once the instrument was returned, we repeated a series of experiments completed in June 2001 to test the sampling efficiencies of the APS 3321 and the SMPS 3934. Aerosols of various sized polystyrene latex beads were generated to verify the sizing accuracy and the sampling efficiencies of the particle sizing instruments in the overlapping region of 0.5 – 1.0 μm. According to TSI, the upgrade enhancements provide greater small-particle sizing efficiency, improved accuracy of mass-weighted distributions, and virtual elimination of false background counts. The results from these experiments are currently being analyzed and will be presented in a future report. The APS and SMPS were reinstalled at the North Birmingham monitoring station March 14.

The computer at the North Birmingham site designated to capture data sets from each instrument experienced electrical difficulties on February 18. These difficulties caused major damage to the motherboard and power supply, which needed to be replaced. In the interim, a laptop computer was used to acquire the data until the main computer was fixed and installed. Two weeks after the main computer was fixed and installed, we continued to have difficulties with the upgraded motherboard communicating with our software and hardware. Again, the computer was removed from the site and a new hard drive was added to communicate more effectively with the motherboard. Since we were able to quickly deploy the laptop computer, we had minimal data loss.

Through routine monitoring of the pressures and flows in the 8400S, on February 27 we noted sample flow measurements were erratic along with a dramatic decrease in vacuum pressure within the instrument. On testing the vacuum pump, it was determined the vacuum pump was not working to its full potential. The pump was removed and replaced with an extra pump from the SRI laboratory. The original 8400S vacuum pump was rebuilt using a kit from the manufacturer and reinstalled on March 8. Three weeks after the rebuilt pump was installed, the vacuum pressure within the instrument again became unstable. Through close examination of the pump, we found the head of the screw attached to the piston had been sheared off resulting in irreparable damage to the pump. An extra pump again replaced the original while a new pump was on order.

Results and Discussion

Hourly averages of the continuous particulate measurements during the quarter are presented in

Figures 1 - 6. The data are plotted together for a meaningful comparison between instruments and data sets. The figures contain the $PM_{2.5}$ mass concentrations measured by the TEOM, 8400S sulfate monitor and integrated size fractions measured by the particle sizing devices. Included are total (submicron) mass concentration as derived from the SMPS measurements, and integrated mass concentrations in the 1 - 2.5 and 2.5 - 10 μm size ranges from the APS measurement data. The $PM_{2.5}$ light scattering extinction coefficient as measured by the M903 nephelometer is plotted on the second Y-axis. In addition, hourly average PM_{10} concentration data were obtained from the Jefferson County Health Department as measured by the county TEOM monitor at the site.

Figures 1 - 3 display the variables associated with the measurements in the fine particulate region. The data sets displayed are the $PM_{2.5}$ TEOM, SMPS total concentration, the 1 - 2.5 μm APS fraction, the 8400S sulfate monitor and the M903 nephelometer. The figures present the same five variables over the months January, February, March, respectively. Figures 4 - 6 represent the variables associated with particulate measurements in the coarse size region, including the PM_{10} TEOM and the 2.5 – 10 μm APS fraction, as well as the $PM_{2.5}$ TEOM concentrations for reference.

APS Comparisons

As described above, the APS 3320 was sent to TSI to be upgraded to an APS 3321 January 23 and reinstalled at the site in mid February after laboratory characterization experiments. Since the SMPS was removed shortly afterward, only limited field comparisons of the two sizing instruments were possible during the quarter. Since one of the promises of the upgrade enhancements was to provide greater small-particle sizing efficiency, we inspected the small amount of available comparison data for indications that these improvements were realized. As indicated below, preliminary indications are encouraging in this regard.

Figure 7 presents a comparison of integrated mass concentrations measured by the SMPS to those measured by the APS 3320 for their common size region between 0.5 and 1 μm. The figure covers the period of Jan 18-21, 2002, immediately before return of the APS for upgrade. While comparison of the two devices over this size range is sensitive to the detailed size distribution and to the assumed particle density, it is clear that the APS 3320 results are lower than the corresponding SMPS values by factors of 5 or more. The same conclusions are clear in the upper traces plotted on the secondary axis, where the data from both sizing devices are normalized to the total $PM_{2.5}$ concentrations measured by the site TEOM. While the ratio of the SMPS integrated size fraction to the TEOM total $PM_{2.5}$ varies between 10 - 20 percent, the corresponding APS 3320 ratios lie in the 1-4 percent range.

Figure 8 presents analogous data for a three day period from February 15-18 using the upgraded APS 3321. During this period, the integrated mass concentrations from the SMPS and the upgraded APS are much more comparable in magnitude. While there are now indications of possible systematic differences for different time periods, the large overall bias of Figure 7 seems now to be rectified. The same conclusion holds in the upper traces where the data from both sizing devices are normalized to the total $PM_{2.5}$ concentrations measured by the site TEOM. Here both devices now show ratios in the 10 –20 percent range previously characteristic

of the SMPS data. In Figure 9 the comparable integrated mass concentrations for the two pairs of devices are presented as scatter plots. The lower efficiency of the 3320 is clear from the plot, as is the more general comparability of the upgraded APS. While the mean regression slope of the 3321 data is only 0.7, the plot suggests that at lower particle concentrations the comparisons lie close to a 1:1 line while the APS lies systematically lower for SMPS values in the 3-10 $\mu g/m^3$ range.

As stated above, these results are preliminary and based on only limited comparisons. The APS and SMPS were reinstalled at the North Birmingham monitoring station March 14 after repair of a failure of the SMPS CPC, and the two devices will be compared in more detail onsite in the coming quarter. The results from these further comparisons and the laboratory experiments described above will be presented in a future report.

Source Attribution Studies

During the quarter preliminary data analysis and modeling studies were conducted to test the potential of the North Birmingham site data for source attribution analyses. Our initial assessment has continued to be optimistic in this regard due to the location of the site relative to several important classes of local and midrange emission sources. The maps in Figures 10-11 show some of these sources. As shown in the metropolitan area map in Figure 10, there are three major coal-fired utility stations in the vicinity of Birmingham, located at distances and bearings, respectively, of 24, 39, and 48 km, and 292, 263, and 136 degrees, relative to North. Also shown are some sources to the southwest of the site associated with the iron and steel industry, including a coke plant, steel plant, and steel pipe mill. The locations of the major highways and metropolitan center indicate that mobile source emissions over a large range of directions will impact the site. Figure 11 provides a more detailed view of the area within 5-8 km of the monitoring site, showing several local industrial emission sources. As the figure shows, the North Birmingham site is centrally located relative to these sources, promising good separation of the contributions of at least three clusters of sources with changes in wind direction. Roughly in a line to the Northeast (bearing about 45°) are two coking plants, a mineral fiber plant, and a cast iron pipe foundry. To the Southeast (bearing from 115-135°), another mineral fiber plant and two iron and steel sources are located within 3 km of the site, roughly in line with one of the coal-fired power plants. Toward the Southwest (bearing from 230-245°) are the iron and steel industry sources shown in Figure 10, as well as a cast iron pipe mill 2-km distant. No significant local sources lie in the West to Northwest quadrant containing the remaining two coal-fired power plants.

Further discrimination of source classes in these directional clusters should be possible using the available compositional information from the continuous gas and particulate monitors. The simultaneous sulfate and SO_2 data available form the R&P 8400S should be especially useful in this regard, since major sources of SO_x are relatively limited, and expected to primarily indicate coal combustion. An indication of the potential usefulness of SO_2 as a tracer species can be found in the directional data in Figure 12. This figure depicts the distribution of 10 minute average wind direction values (binned in 10° increments) corresponding to valid 8400S measurements during the period from July 2001 to January 2002. The measured wind direction frequency does not show a dominant prevailing direction, though frequencies are enhanced in the

30° - 240° directions followed by the local topography. Also plotted is the fraction of measurements for each directional bin having SO_2 concentrations greater than 12 ppb. This measure has a strong directional signature. The two peaks centered near 300° and 270° strongly suggest the two nearest coal fired utility plants; the third plant undoubtedly contributes as well to the peak at 125°, but the height of this peak and of the broad frequency contribution below 90° suggest that the local industrial sources also contribute strongly to the number of high SO_2 events from these easterly directions.

To further explore the contributions from individual sources using SO_2 peaks as tracers, individual events during the summer of 2001 were surveyed. Figure 13 shows three such characteristic events during the period July 10-15. In the figure are plotted the SO_2 and particle sulfate channels of the 8400S, corresponding 10 minute averages of the local mean wind direction and of the $PM_{2.5}$ mass concentration from our TEOM, as well as averages of the CO and NOy* signals from the SEARCH monitors. The first such episode in the figure is the series of SO_2 peaks on the morning of July 10 accompanied by significant peaks in reactive nitrogen species but no corresponding increase in CO, PM sulfate or $PM_{2.5}$ mass concentration. Trajectory analysis indicates the likely source of SO_2 in this air mass to be the nearest coal-fired power plant at 293°. The measured gas and particulate species profile is also consistent with the fresh plume of a typical coal-fired power plant.

Also highlighted in Figure 13 are two high SO_2 episodes on July 15. The first episode occurs during the morning hours, in which a series of SO_2 peaks occur. While NOy* signals generally track all these SO_2 peaks, other pollutant measures do not, and fluctuate over much of this time period. However, the central SO_2 peaks at 3:20 and 4:50 AM (CST) show clearly corresponding peaks in CO, PM sulfate and $PM_{2.5}$ mass concentration, suggesting a distinct, combustion-related source of the SO_2 in these time periods. Backwards trajectories during this time range lie in the quadrant to the northeast of the site, where are located the collection of sources described above, including two coke plants. It is likely that the measurements currently available at the site can track this source type, even in proximity to other plants of other industrial classes.

The third episode is a relatively isolated SO_2 peak between 4:10 and 7:00 PM on the same day, which occurs without corresponding changes in NOy* or CO levels, but is accompanied by corresponding peaks in $PM_{2.5}$ mass concentration, and specifically in PM sulfate. Integrated concentration measurements of these three species show that the sulfate peak, as sulfate ion, would account for 77% of the added mass in the $PM_{2.5}$ mass concentration. This high fraction places stoichiometric constraints on the possible sulfate species involved, since the counterions per sulfate must have total molar weight less than about 30. Reasonable candidates are sulfuric acid, or ammonium bisulfate, or less probably $NaHSO_4$. A candidate fully neutralized sulfate species is $MgSO_4$, but it is not clear that the 8400S would detect sulfate from either of these two inorganic salts with reasonable efficiency. As might be anticipated, the SEARCH continuous carbon instruments (R&P 5400 and aethelometer) show no increase in particulate carbon corresponding to the mass peak. In short, the source origin of the third episode is not completely clear. The air mass over this time period passed through a broad band of the Southeast quadrant before reaching the site, passing near (but not directly over) the nearby cluster of sources; however, the composition of the particulate species does not seem typical for them. We are searching for other occurrences of similar events for comparison.

Since our particle sizing instruments were operating during the last two of these episodes, we were able to investigate changes in the particle size distribution which may be characteristic of the specific emission sources attributed to the events. Figure 14 shows particle mass concentrations in several size bands over the period covered by Figure 13. Over the entire period, including the two episodes, most of the particulate mass falls in the two submicron size bands of 120-300 nm and 300-500 nm. The smaller (120-300 nm) of these size fractions dominates in the morning episode, and to a lesser extent, in the background period before and afterwards. In contrast, the 300-500 nm fraction is comparable in magnitude during the afternoon event, and slightly greater in the background period before and after this episode. (Similar shifts in the size fraction can be seen in the earlier broad episode of high particulate levels from July 11-13). In Figure 15 the SMPS size distribution for the two July 15 episodes is shown in more detail. During the morning episode (event 1) a broad background size distribution peaked at roughly 60 nm (number basis) is supplemented by a similarly broad distribution from the event. The net event size distribution calculated from background subtraction is peaked near 80 nm, and appears to be sparse above 300 nm. The afternoon episode (event 2) shows a more clear contrast between an aged background aerosol predominantly larger than 200 nm and a narrower event size distribution peaked around 120 nm. The figure shows a mode at larger particle diameter for the second event and not the first; however, these features are less certain due to the uncertainty in the changing background near the events, complicated by an intervening period of instrument outage. In any case, the figure demonstrates that event particle size distributions may be determined for favorable cases, will have some utility in characterizing the primary particulate from local sources, and may add a useful variable to assist in source attribution receptor analysis.

Conclusions

Data collected in this quarter continue of the seasonal trends from previous quarters. The next quarterly report will reflect a full year of data for the full set of instruments in the current sample shelter. The source attribution studies begun last quarter will be extended and augmented by PMF receptor model analysis using the continuous data sets. We anticipate that these analyses will provide good separations of the effects of major source classes and of spatial source clusters, and will provide useful information relevant to $PM_{2.5}$ implementation strategies.

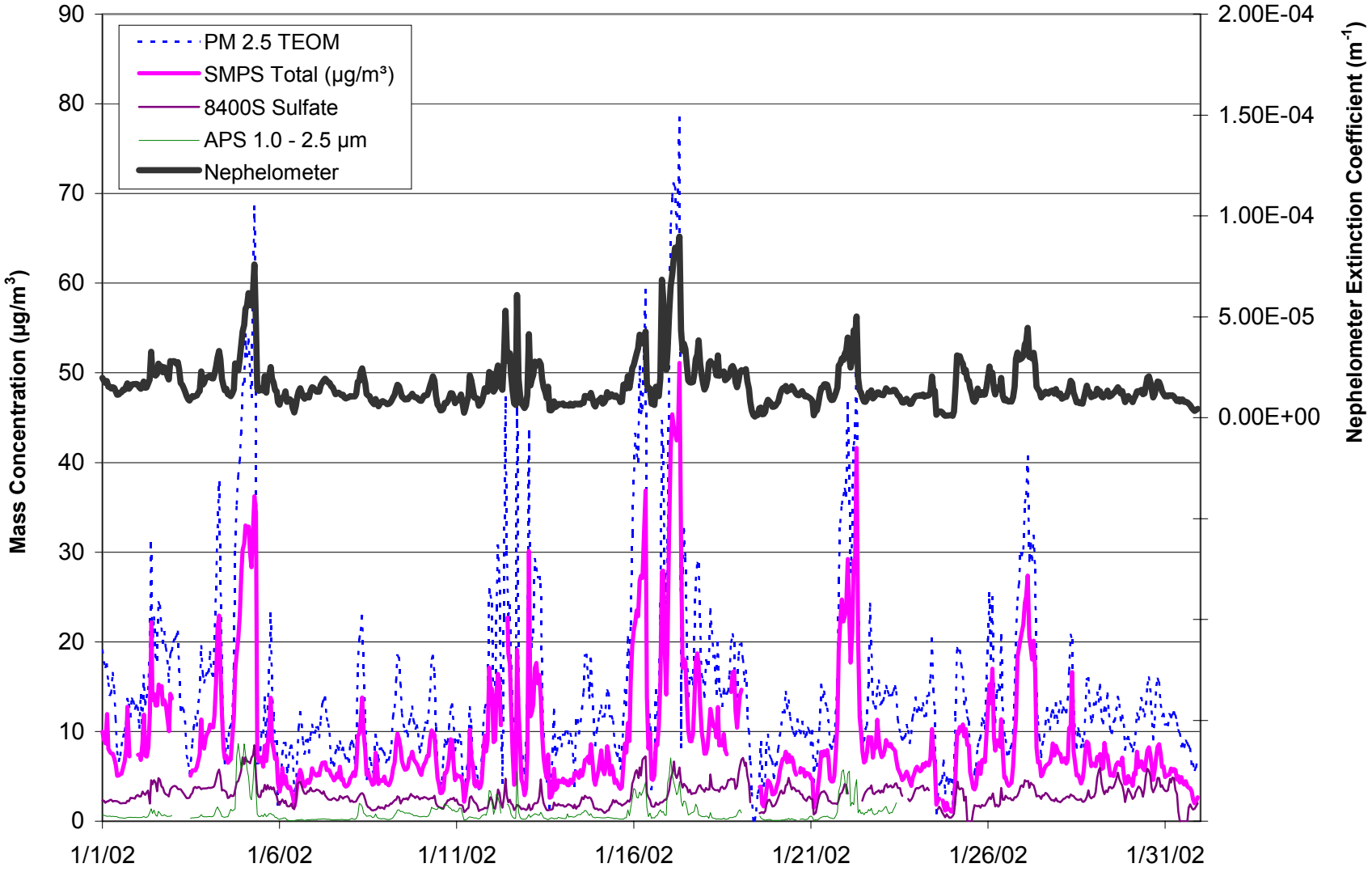

Figure 1. Hourly averaged fine particle data from the North Birmingham site during the period of January 1 – January 31, 2002.

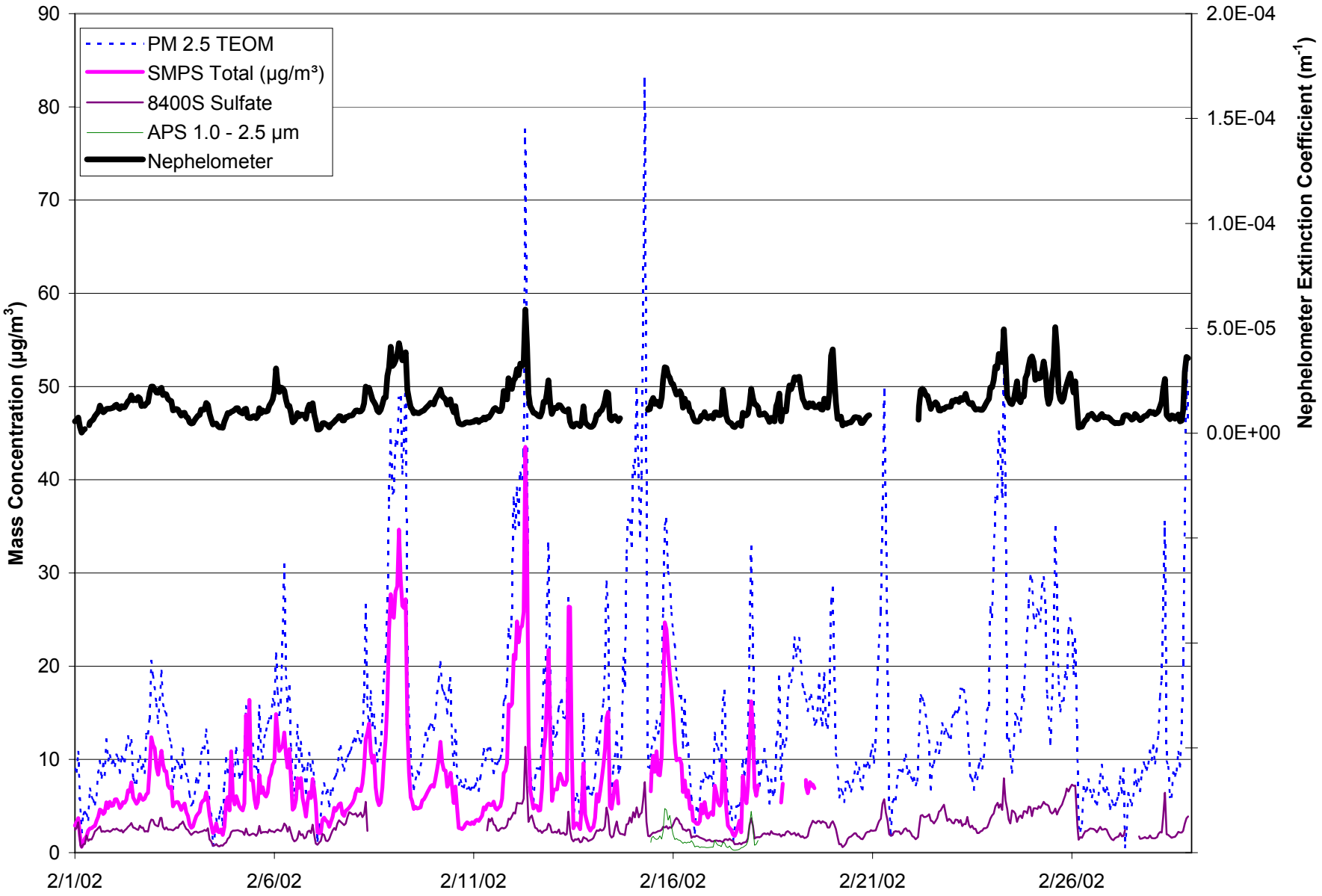

Figure 2. Hourly averaged fine particle data from the North Birmingham site during the period of February 1 – February 28, 2002.

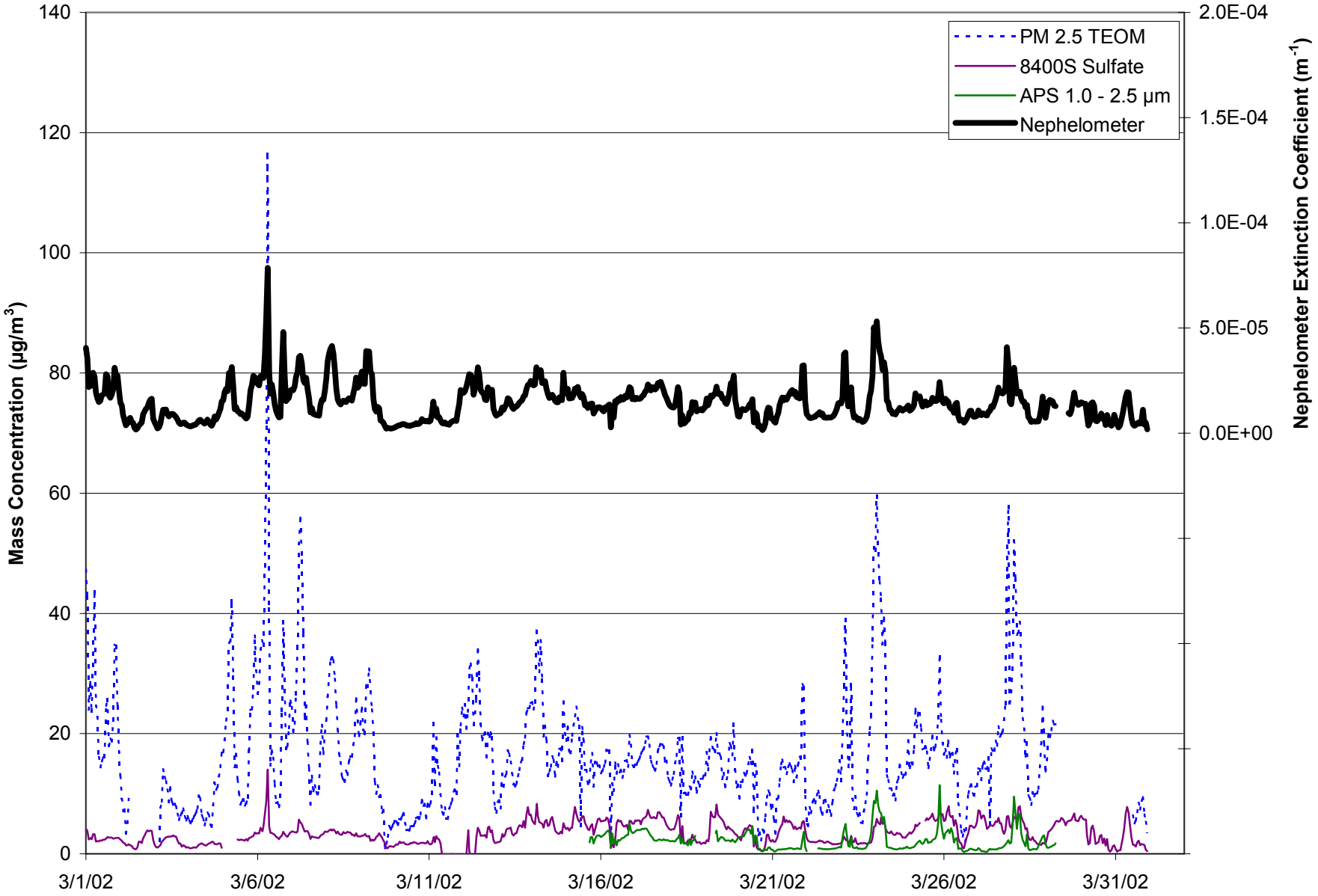

Figure 3. Hourly averaged fine particle data from the North Birmingham site during the period of March 1 – March 31, 2002.

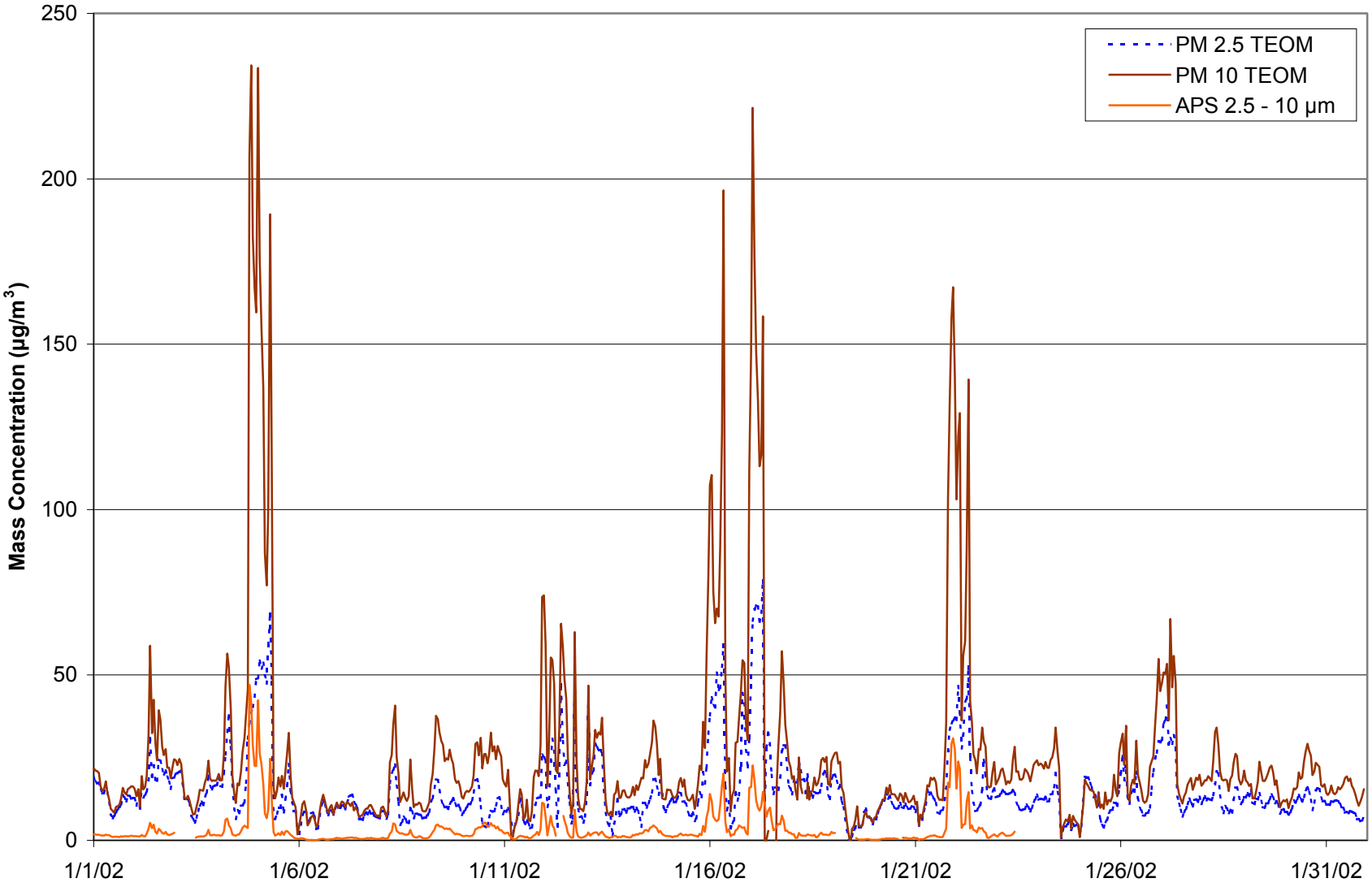

Figure 4. Hourly averaged coarse particle data from the North Birmingham site during the period of January 1 – January 31, 2002. Also included are PM_{10} concentrations reported by Jefferson County.

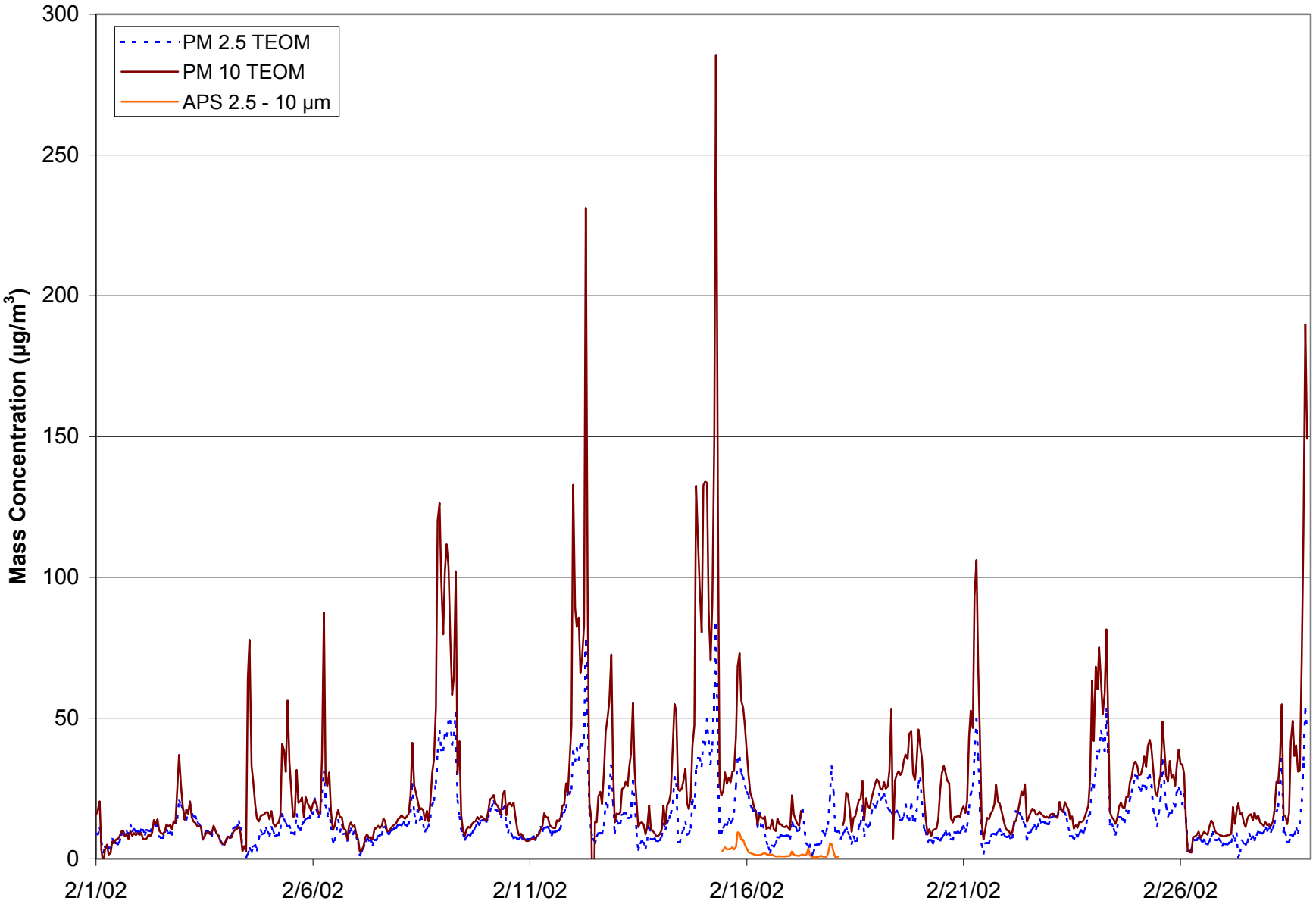

Figure 5. Hourly averaged coarse particle data from the North Birmingham site during the period of February 1 – February 28, 2002. Also included are PM_{10} concentrations reported by Jefferson County.

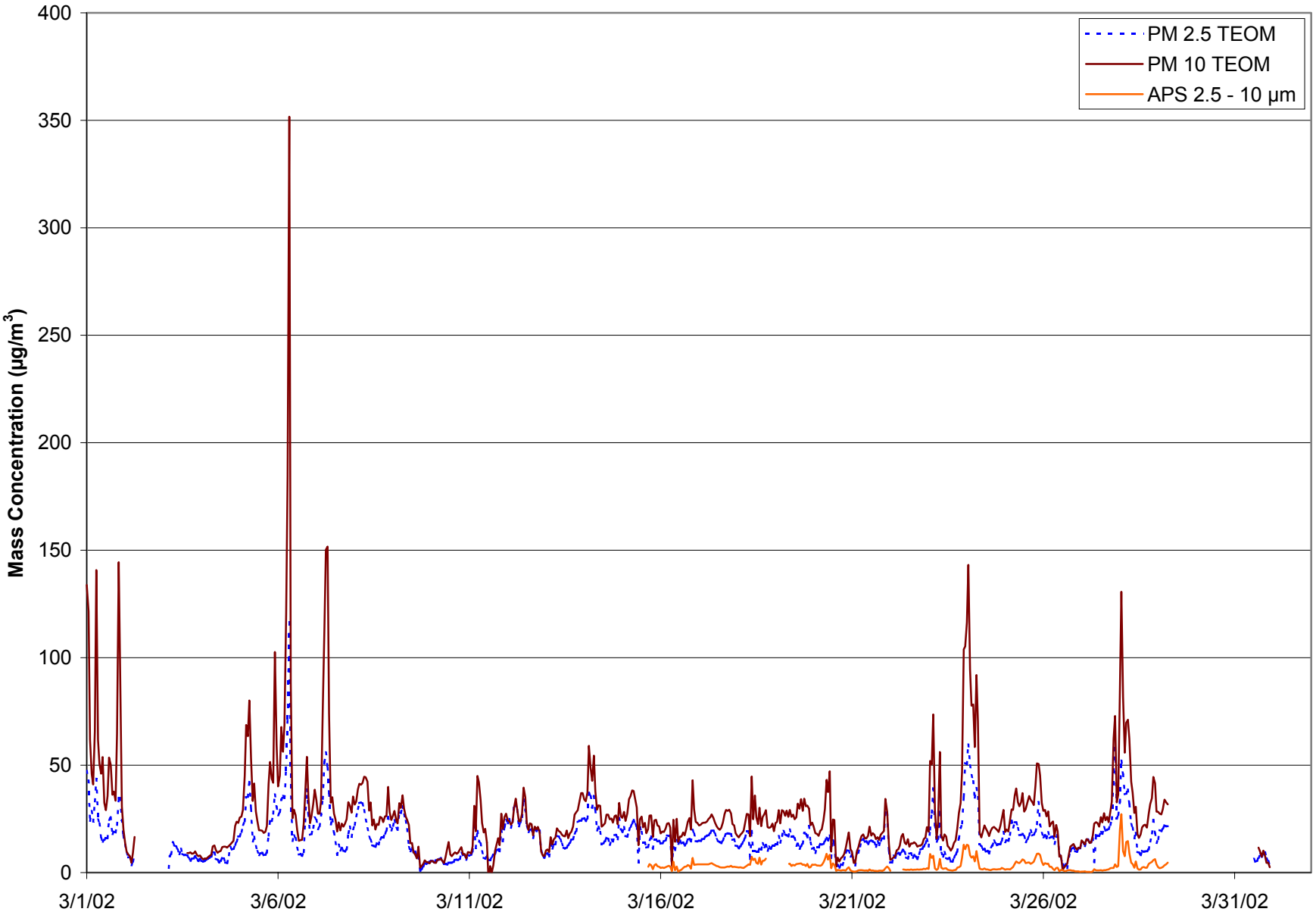

Figure 6. Hourly averaged coarse particle data from the North Birmingham site during the period of March 1 – March 31, 2002. Also included are PM_{10} concentrations reported by Jefferson County.

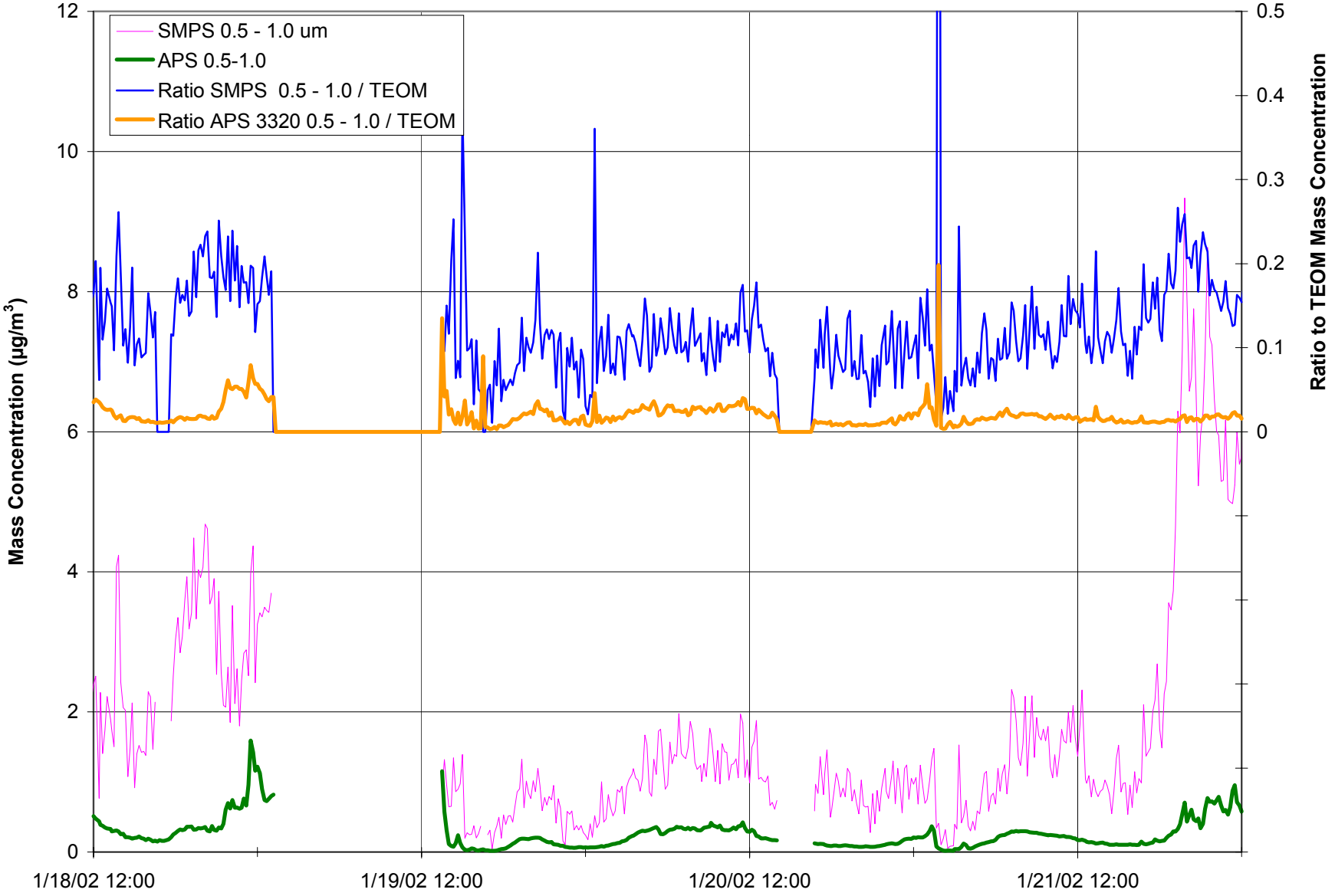

Figure 7. Comparison of the APS 3320 and SMPS 3394 mass concentrations in the overlapping size region of 0.5 - 1.0 µm for January 18 – 21, 2002. The secondary Y-axis presents the ratio of the particle size instrument mass concentrations normalized to the $PM_{2.5}$ mass concentration.

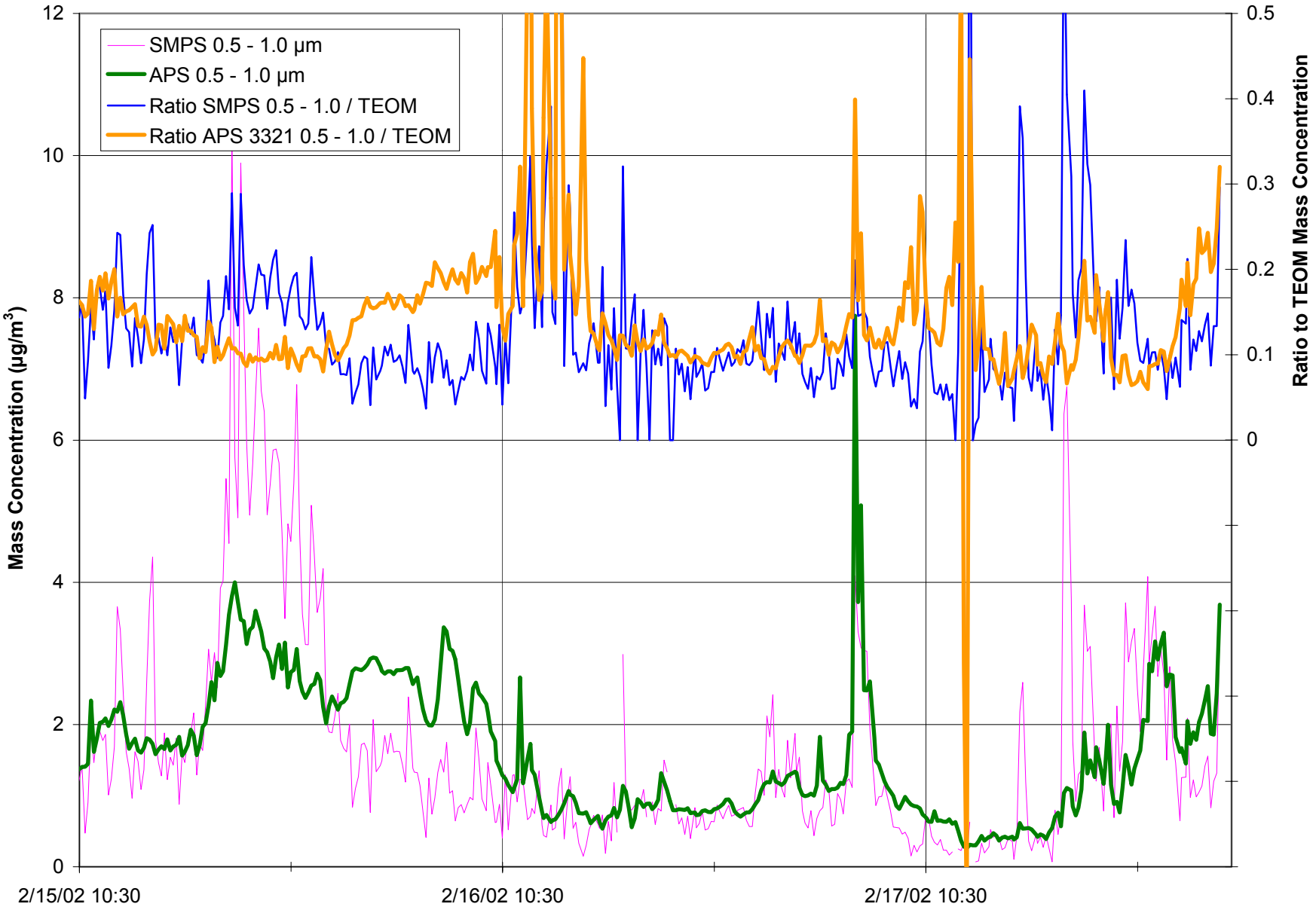

Figure 8. Comparison of the APS 3321 and SMPS 3394 mass concentrations in the overlapping size region of 0.5 - 1.0 µm for February 15 – 18, 2002. The secondary Y-axis represents the ratio of particle size instrument mass concentrations normalized to the TEOM $PM_{2.5}$ mass concentration.

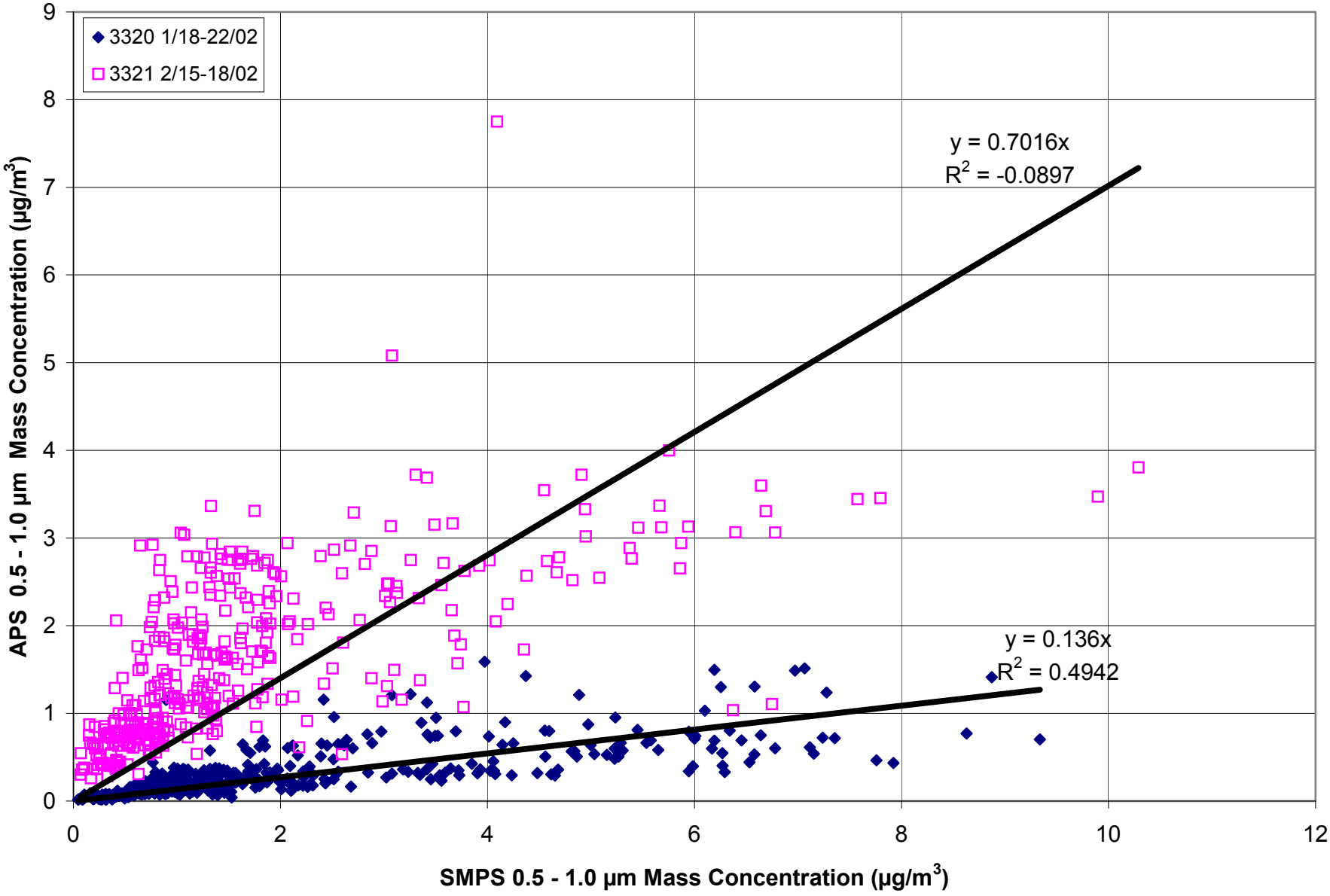

Figure 9. Comparison of the APS 3320 and upgraded 3321 to the SMPS 3934 concentrations in the 0.5 - 1.0 µm size region.

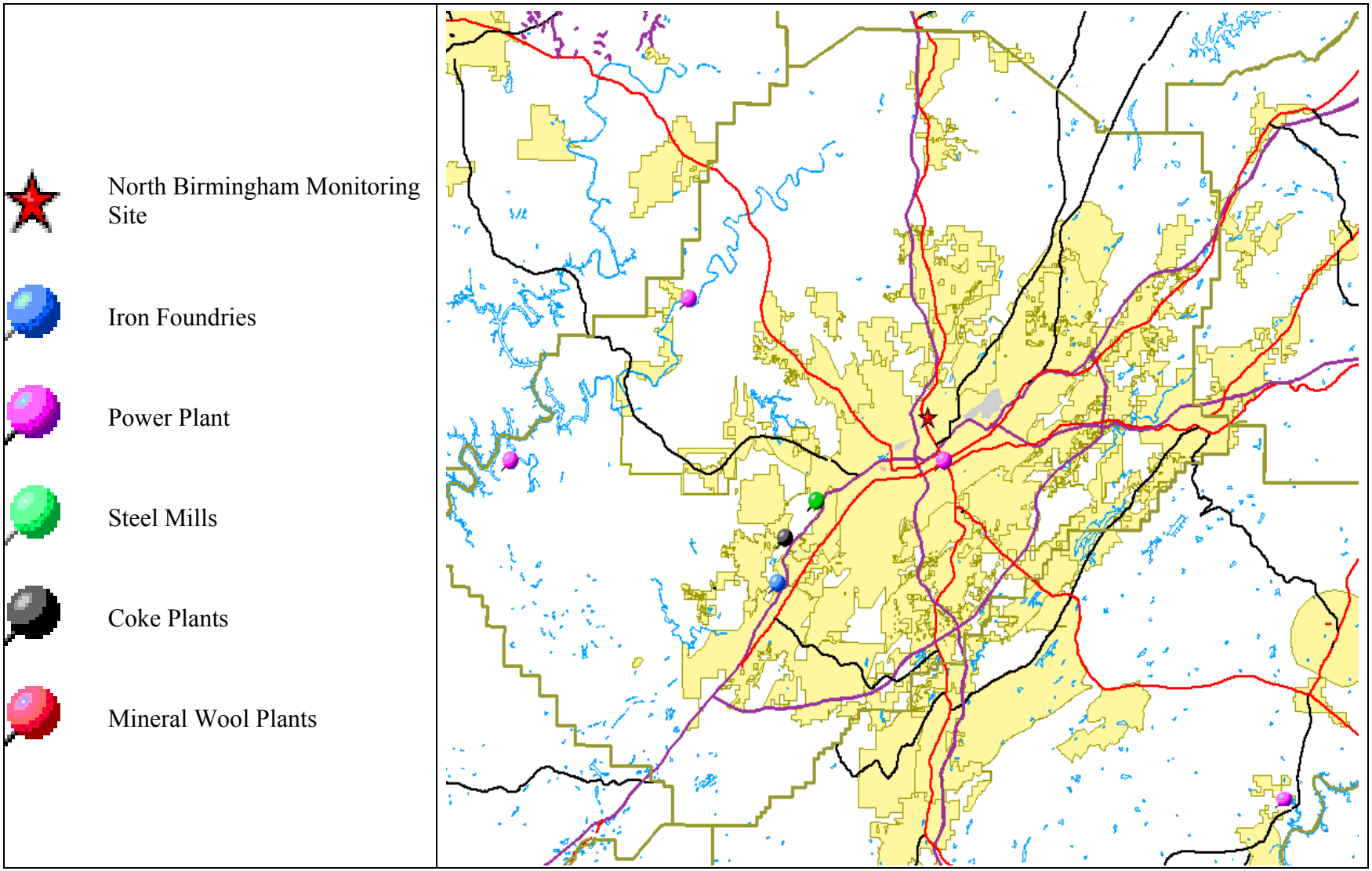

Figure 10. Map of Birmingham Metropolitan Area showing N. Birmingham site and sources outside of the city limits.

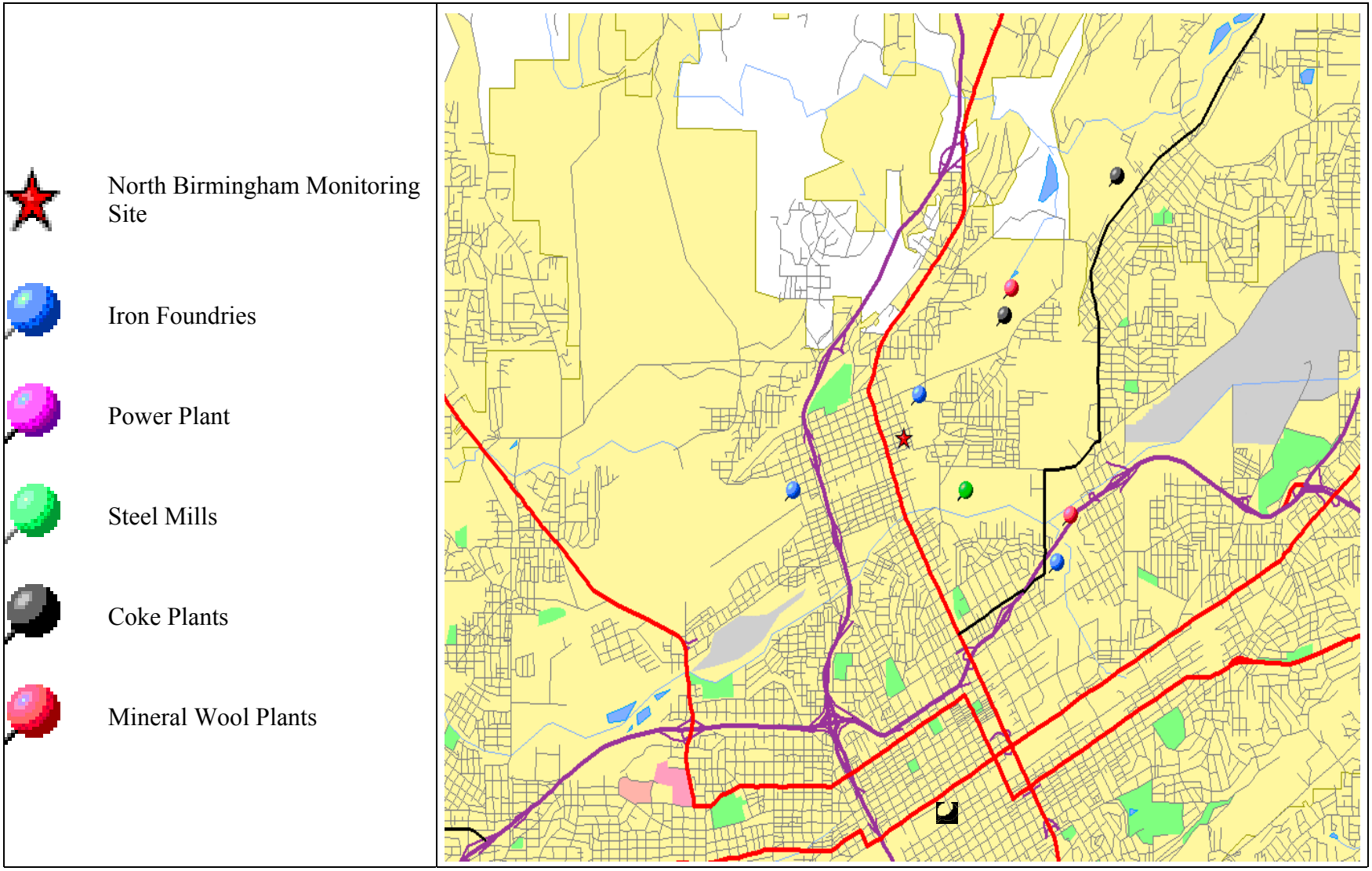

Figure 11. Expanded map of Downtown Birmingham showing monitoring site and local industrial sources.

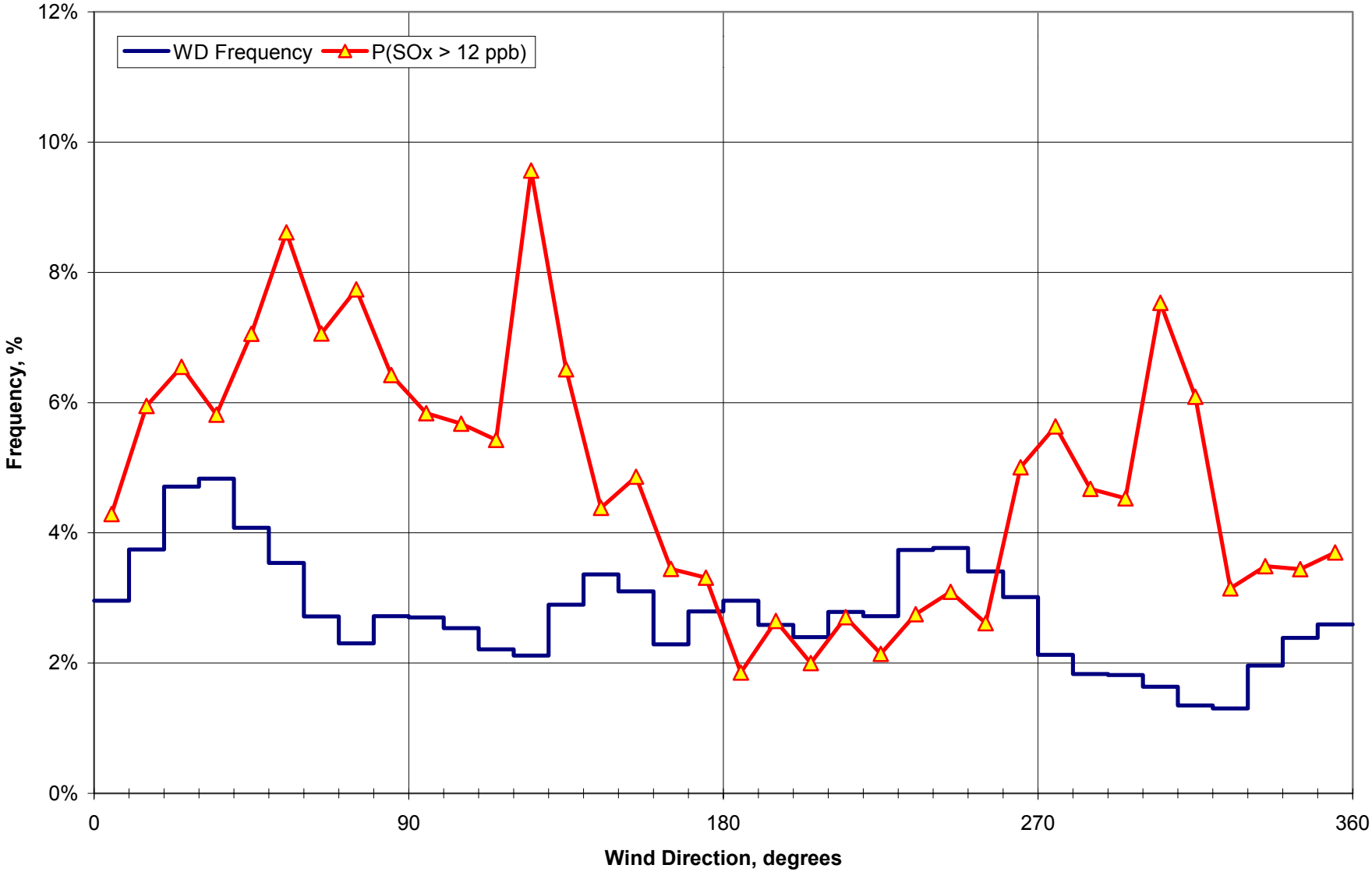

Figure 12. Ten minute average wind direction values (binned in 10 degree increments) corresponding to 8400S data from July 2001 through January 2002.

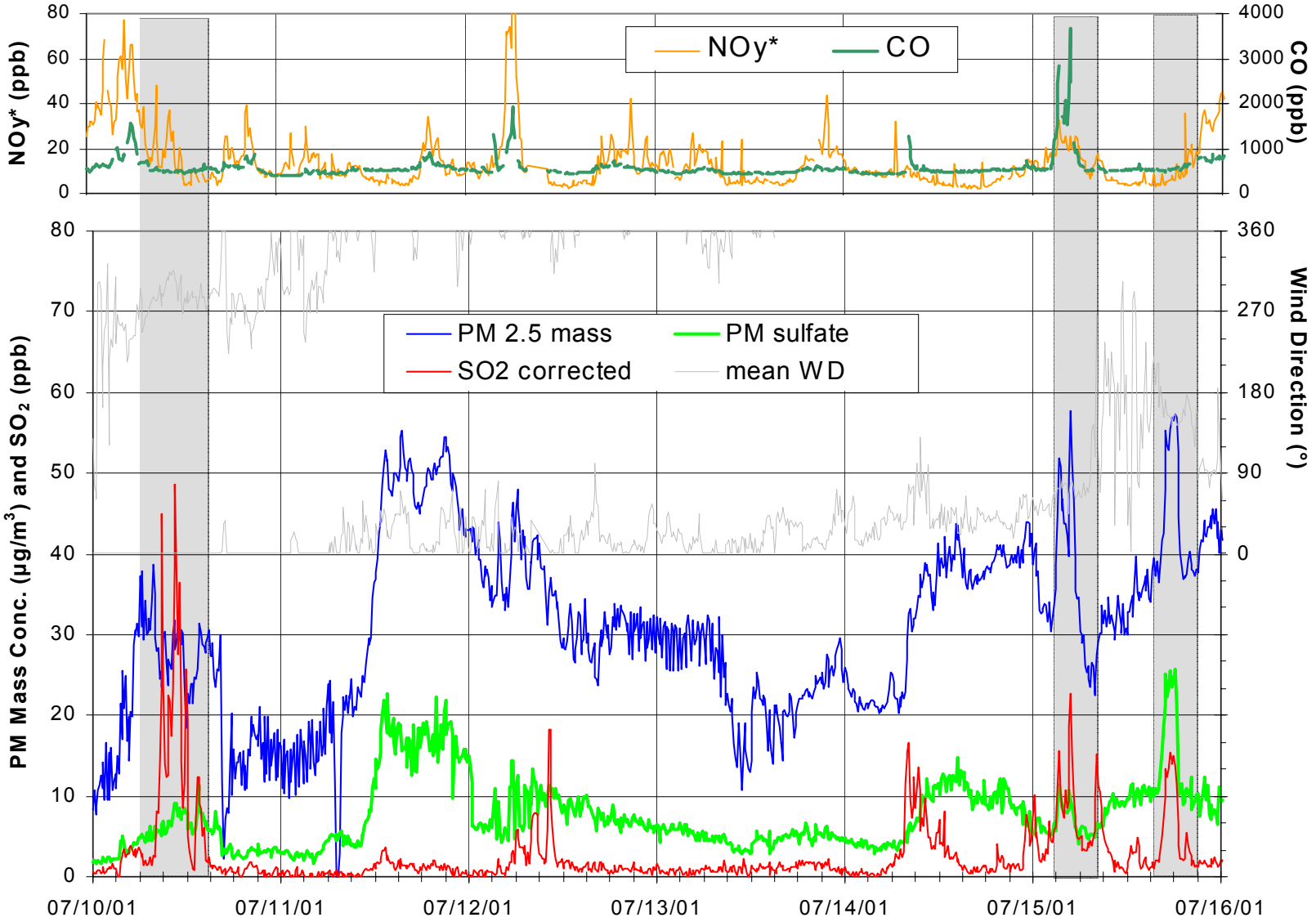

Figure 13. Three individual episodes during July 10 – 16, 2001 analyzed for source identification utility.

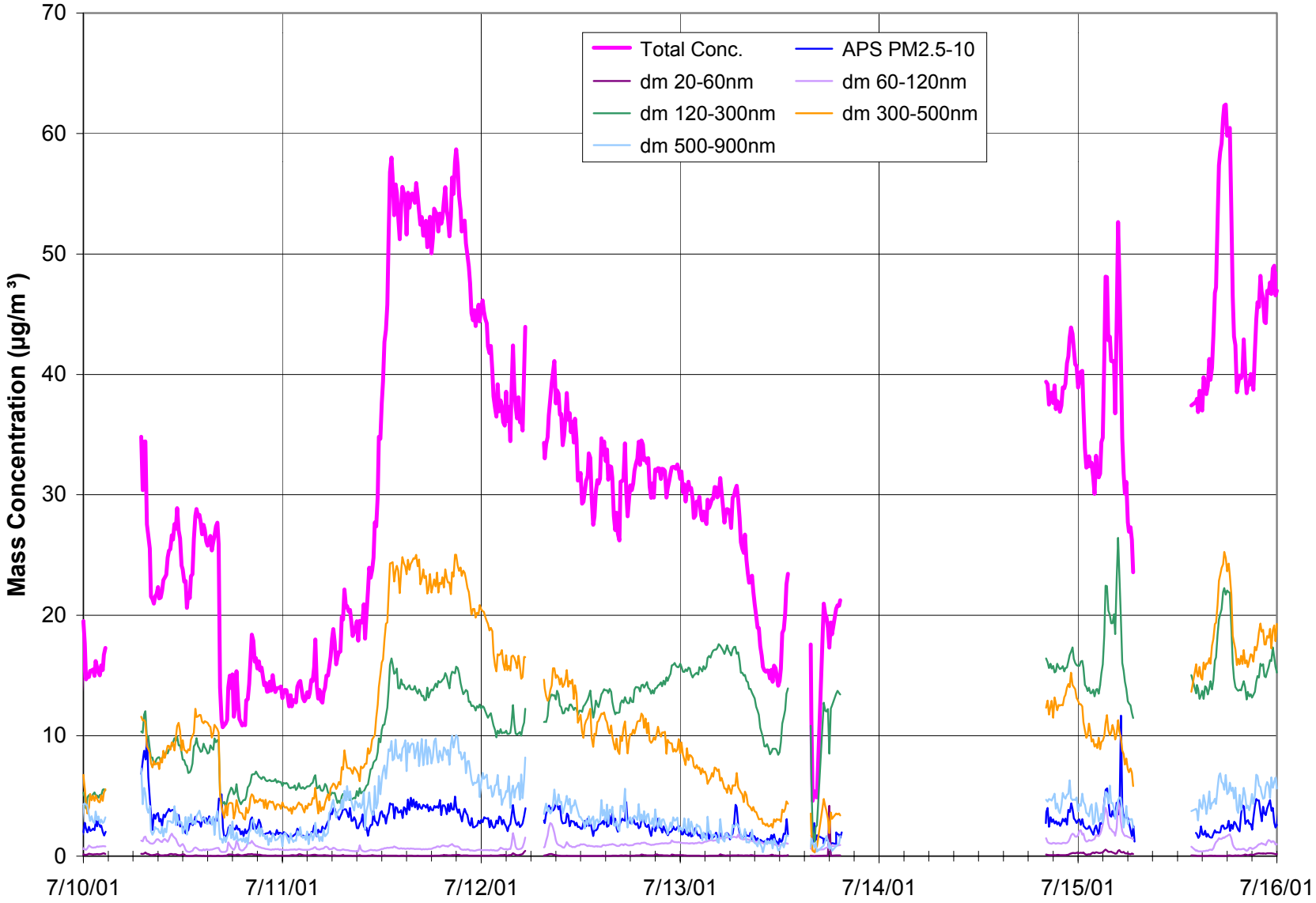

Figure 14. Measured particle mass concentrations in several size bands during July 10 – 16, 2001.

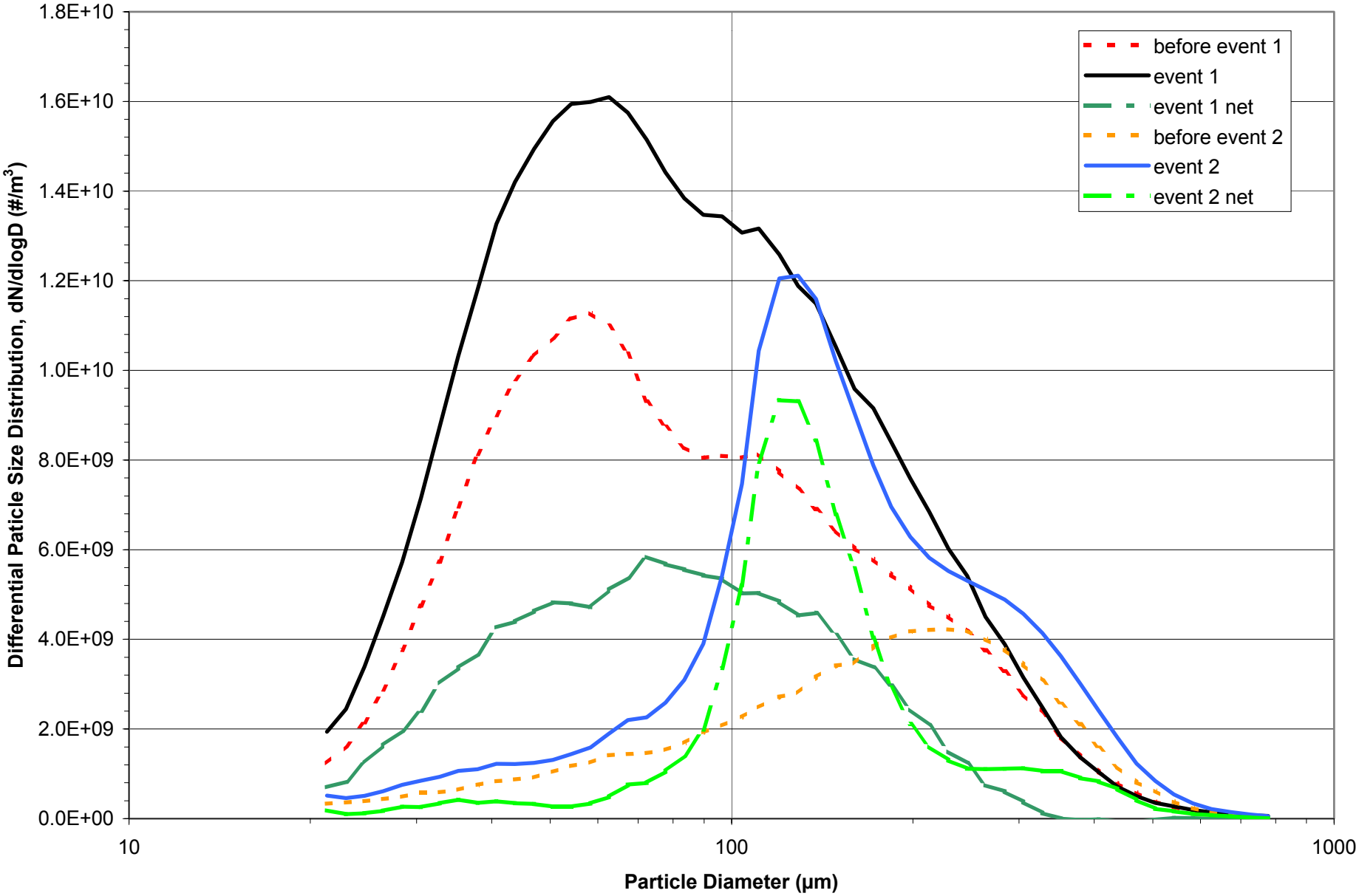

Figure 15. SMPS differential number size distributions for two individual events on July 15, 2001